

SPECTROSCOPIC STUDIES OF LEWIS ACID-BASE COMPLEXES

III: *Vibrational Frequencies, Assignments and Normal Coordinate Analyses for Isotopic Varieties of Phosphine Borane and Trifluorophosphine Borane*

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Abstract. Vibrational spectra of the two Lewis complexes, phosphine borane, PH_3BH_3 , and trifluorophosphine borane, PF_3BH_3 , have been investigated for several isotopic species preserving C_{3v} symmetry. New assignments are proposed and substantiated by normal coordinate analyses formulated in the compliance constant basis.

1. Introduction

Phosphine borane and trifluorophosphine borane are both weak Lewis type complexes which have been of interest to chemists in recent years. The nature of the bonding between the two halves of the molecules has been the subject of considerable discussion and two models have been proposed to describe the dative bond. One has been termed the borane hyperconjugative model [1] and the other the dipole moment-polarizability model [2]. The essential features of each model have been summarized recently by Cowley [3]. Normal coordinate analyses of the vibrational spectra of these molecules may be expected to provide information useful in discussing the merits of these two models. However, the spectroscopic data available in the literature have been somewhat limited, assignments have not been entirely certain and experimental molecular parameters have not been available until recently. Consequently, the force constant values which have been cited [4, 5] in various discussions have had a higher degree of uncertainty than desirable.

The unexpected coordinating ability of trifluorophosphine towards boron hydrides was first demonstrated by Parry and Bissot [6] in 1956 with their synthesis of the borane adduct. Structural evidence was provided by the vibrational Raman spectra [7] of PF_3BH_3 and PF_3BD_3 which were most easily interpreted in terms of a C_{3v} ethane-like structure having a P—B dative bond. This early structural inference was verified some time later by a microwave study [8] which provided values for the molecular parameters. No infrared data have appeared in the literature, the only vibrational frequencies available being those from the original Raman work.

The existence of phosphine borane has been known for a much longer time [9] than the trifluorophosphine adduct but its molecular and spectroscopic properties have received less attention until recently. The first structural information in the literature is provided by an X-ray study [10] which established the presence of a p—B bond and gave a value for its length but did not locate hydrogen atoms. A later spectroscopic

and NMR study [11] confirmed molecular C_{3v} symmetry while quite recently, microwave results have been presented [12] giving molecular parameters. Raman and infrared data for PH_3BH_3 were reported by Rudolph, Parry and Farran [11] while similar data for PH_3BD_3 , PD_3BH_3 and PD_3BD_3 have been published by Davis and Drake [13].

The present work has extended the experimental results for trifluorophosphine borane to include Raman and infrared data for the normal and boron-10 isotopic species as solids at low temperatures and also includes the infrared spectrum of the gas. In the case of phosphine borane, Raman data are presented for the liquid and solid phases of three deuterated isotopic species preserving C_{3v} symmetry. The new data together with the results of a normal coordinate analysis have removed most of the uncertainties from the assignments of both compounds.

2. Experimental

2.1. PREPARATION AND PURIFICATION OF COMPOUNDS

Trifluorophosphine was prepared by fluorinating PCl_3 with ZnF_2 [14]. The product was purified by passage through ion exchange resin to remove HCl and then fractionally distilled using standard vacuum line techniques. Diborane containing the natural mixture of boron isotopes was obtained from the Callery Chemical Co. Isotopically enriched species of diborane were prepared by the reduction of the appropriate boron trifluoride etherate by lithium aluminum hydride or deuteride. The LiAlD_4 was specified as 97 atom percent deuterium, the boron-10 etherate contained 92 atom percent ^{10}B and the boron-11 etherate contained 99.4 atom percent ^{11}B . Phosphine was prepared by the pyrolysis of phosphorous acid while the deuterated phosphine was prepared by the hydrolysis of calcium phosphide with heavy water.

Trifluorophosphine borane was prepared by the direct reaction of diborane with a five-fold excess of PF_3 following the method of Parry and Bissot [6]. Phosphine borane was prepared by the reaction of liquid phosphine and liquid diborane at -105° after which unreacted and volatile materials were pumped off [11]. In addition to dissociating readily, these complexes also react readily with traces of water and other impurities. Very careful handling and absolute cleanliness in the vacuum line were necessary for the successful preparation of the spectroscopic samples.

2.2. SPECTROSCOPIC EQUIPMENT AND PROCEDURES

The earlier portion of the infrared work was completed with a Perkin-Elmer Model 21 spectrophotometer equipped with CaF_2 , NaCl and KBr prisms. Later work was carried out with a Beckman IR-12 instrument. In the case of trifluorophosphine-borane, solid films were prepared by spraying vapor evaporating from the liquid at -126° directly onto a NaCl or KBr plate held at liquid nitrogen temperatures. The sample plate was in good thermal contact with a copper block forming the bottom of the liquid nitrogen reservoir and the whole was contained in an evacuated *T*-shaped container of conventional design. Films of phosphine-borane were prepared in a

similar fashion by sublimation. Since the preparation of the sample film could be done in the spectrophotometer, the process could be stopped when a film reached optimum thickness. Vapor spectra of PF_3BH_3 were obtained in a 7.5 cm cell with CsI windows. To reduce decomposition, a reservoir of liquid at -126° was attached to the cell and the spectra were obtained as rapidly as possible.

Raman spectra of solid PF_3BH_3 were obtained photographically using a Gaertner two prism spectrograph with a dispersion of approximately 180 cm^{-1} per mm in the blue region and a resolution of about 10 cm^{-1} under the conditions of the experiment. Details of the experimental arrangement have been described elsewhere [15]. Raman spectra of phosphine borane were recorded with a Spex Model 1401 Ramalog using either the 6328 Å line of a helium-neon laser or the 4880 Å line of a 600 mW argon ion laser with the samples sealed into evacuated 1 mm capillaries.

Uncertainties in the frequencies for well defined and reasonably sharp bands are estimated to be about 1 cm^{-1} for both the Raman and infrared data. Those for the weaker and more diffuse bands range from 2 to 5 cm^{-1} . Raman spectra were calibrated using argon lines while the Beckman IR-12 spectrometer had been calibrated over its range with standard substances and the scale found to be accurate to within 0.2 cm^{-1} .

3. Experimental Results and Assignments

3.1. TRIFLUOROPHOSPHINE-BORANE

Infrared frequencies for gaseous PF_3BH_3 (natural boron) and for solid PF_3BH_3 and solid PH_3BH_3 are listed in Table I. Listed in the same table are Raman data for solid PF_3BH_3 and $\text{PF}_3^{10}\text{BH}_3$. For comparison, the Raman data from the literature [7] have been added.

The vibrational frequencies of ethane-like molecules having C_{3v} symmetry classify into $5A_1 + 1A_2 + 6E$ modes. The A_1 and E modes are Raman and infrared active while the A_2 mode (torsion) is inactive in both. Although the microwave study [8] was unable to distinguish between the staggered and eclipsed conformations of trifluorophosphine-borane, the staggered appears more likely. The number and symmetry of the vibrational modes, however, does not depend on this distinction. The numbering scheme and an approximate description of the modes is given in Table II.

The vibrational assignments proposed in the initial Raman investigation [7] are generally supported by the results of the present study. The principal difference is in the assignment of the P–F stretching modes. Originally, ν_3 , the symmetric P–F stretch, was assigned to a band at 944 cm^{-1} in the spectrum of PF_3BH_3 while the weak band at 920 cm^{-1} was assigned as a difference band. However, the 920 cm^{-1} band is quite intense in the infrared spectrum and appears to be a better choice for this fundamental. Similarly, the band at 957 cm^{-1} was assigned to ν_9 , the degenerate P–F stretch, but this mode is now reassigned to 944 cm^{-1} , also on the basis of the infrared evidence. The corresponding assignments for the deuterated compound remain unchanged at 944 and 958 cm^{-1} , respectively. As a result of these revised assignments, it is now apparent that the P–F stretching modes shift to higher frequency upon deutera-

TABLE I
Observed infrared and Raman frequencies of three isotopic varieties of trifluorophosphine borane (cm^{-1})

$\text{PF}_3^{10}\text{BH}_3$			PF_3BD_3			Assignments
Raman ($s, -180^\circ$)	Infrared ($s, -180^\circ$)	Raman ^a ($l, -80^\circ$)	Raman ($s, -180^\circ$)	Infrared ($s, -180^\circ$)	Infrared ($g, -126^\circ$)	
2471 ms	2654 vw 2469 m, sh	2655 vvw	2655 vw	2643 w 2459 m, sh	2464 m 2463 m	
2397 s	2456 vs	2455 vs, dp	2460 s	2450 vs	2453 s 2451 s	1845 vs, dp ν_7
2337 vvw, sh	2394 m	2385 vs, p	2392 vs	2391 ms, sh		1717 vs, p ν_1
2243 vvw	2341 w, sh 2239 w 2212 w 2173 w 2137 vw	2328 vvw 2247 vw	2336 sh 2239 vvw	2340 w, sh 2231 w 2197 vw		1602 vw $2\nu_8$
	1831 vw, br 1704 m 1676 vw 1650 vw 1636 vvw 1560 vvw 1542 vvw 1460 vvw 1418 w	2140 vw 2112 vvw	2146 vvw 2113 vvw 1818 vvw	2146 vw		1672 vw $2\nu_2$
1391 vvw	1227 m 1208 vvw 1127 sh		1328 vvw 1314 vw	1703 vw, sh 1681 w 1668 w, sh 1648 vvw 1523 vvw 1447 vvw 1417 vvw, sh 1403 vw, sh 1396 w 1335 vvw 1308 vw 1227 vw 1208 w		$\nu_8 + \nu_{10}$ $\nu_2 + \nu_4$ (^{10}B) $\nu_2 + \nu_4$ (^{11}B) $\nu_3 + \nu_{10}$ $\nu_2 + \nu_{11}$ $2\nu_{10}$ OR $\nu_5 + \nu_9$ $\nu_9 + \nu_{11}$ $\nu_3 + \nu_{11}$ OR $\nu_8 + \nu_{12}$ $2\nu_4$ (^{10}B) $2\nu_4$ (^{11}B)
					1132 w	

Table I (continued)

1127 m	1123 s	1117 s, dp	1124 ms	1121 s	1117 w 1105 w	807 s, dp	ν_8
1092 vvw	1093 w 1078 vw	1077 w, p	1079 w	1079 w, sh 1068 w			$\nu_2^{(10B)}$ $\nu_2^{(11B)}$
972 w	1051 vw 988 m, sh	1040 w, p 957 m, dp	1030 vw 969 m	1032 vvw 957 s, sh	959 vs 951 vvs 943 vvs		$\nu_4 + \nu_5$
944 w	943 vs	944 m, p	939 m	942 vs	931 vvs	958 m, dp	ν_9
925 w	916 s 902 s, sh	920 w, p 886 vw, p?	921 m	919 s 892 w, sh 830 vw, sh 736 vw	922 vs, sh	944 m, p?	ν_3 $\nu_{10} + \nu_{12}$
619 m	736 w 709 s 702 w, sh 613 s 606 s, sh	697 vw	701 vw	709 w, sh 700 ms 616 s, sh 606 s	693 vw 619 w	572 s, p	$2\nu_{11}$ $\nu_{10}^{(10B)}$ $\nu_{10}^{(11B)}$ $\nu_4^{(10B)}$ $\nu_4^{(11B)}$
449 vw	439 s	607 s, p	608 m		609 m 452 w 448 w 442 w 433 w 370 w		ν_5 ν_{11} ν_{12}
		441 m, p 370 vw 197 m, dp	438 w	436 s		421 m, p 362 vw 169 m, dp	

^a s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, p = polarized, dp = depolarized.
s Reference 6.

TABLE II
Approximate description of vibrational modes of PF_3BH_3 and PH_3BH_3

	PF_3BH_3	PH_3BH_3
<i>A</i> ₁ Class		
ν_1	Sym B—H stretch	Sym P—H stretch
ν_2	Sym BH_3 deformation	Sym B—H stretch
ν_3	Sym P—F stretch	sym BH_3 deformation
ν_4	P—B stretch	Sym PH_3 deformation
ν_5	Sym PF_3 deformation	P—B stretch
<i>A</i> ₂ Class		
ν_6	Torsion	Torsion
<i>E</i> Class		
ν_7	Asym B—H stretch	Asym P—H stretch
ν_8	Asym BH_3 deformation	Asym B—H stretch
ν_9	Asym P—F stretch	Asym BH_3 deformation
ν_{10}	BH_3 rock	Asym PH_3 deformation
ν_{11}	Asym PF_3 deformation	BH_3 rock
ν_{12}	PF_3 rock	PH_3 rock

tion. This unusual behavior is attributed to the repelling effect of the BH_3 deformation modes of the same symmetry which lie above the P—F stretching modes in the hydrogen compound but shift to a position below them upon deuteration.

Three fundamentals of the various isotopic species have not been identified. The BD_3 rock of the deuterated molecule was not observed in the original Raman work and this species was not investigated further here. The normal coordinate calculations predict a value of 537 cm^{-1} for this mode. Neither ν_{11} or ν_{12} , the *E* class PF_3 deformation and rocking fundamentals of the boron-10 species, were observed in the present study because of experimental problems. The calculations predict values very close to those of the boron-11 species. A value of 169 cm^{-1} was reported for the lowest fundamental of PF_3BD_3 in the original Raman work. However, the normal coordinate calculations consistently predicted this mode to occur at approximately 184 cm^{-1} suggesting either that a relatively large error is present in the reported experimental value or the assignment is not correct.

The assignments of the fundamentals shown in Table V are supported by the results of the normal coordinate calculations and also by the product rule ratios shown in Table IV.

3.2. PHOSPHINE BORANE

Raman frequencies for PD_3BH_3 , PH_3BD_3 and PD_3BD_3 in the liquid and solid states are listed in Table III and representative spectra of the last two species are shown in Figures 1 and 2. The molecular symmetry and the number and classification of fundamentals is the same as for trifluorophosphine borane. In PH_3BH_3 , the staggered conformation has been confirmed experimentally [12]. The numbering scheme is also given in Table II.

TABLE III
Observed Raman frequencies for three varieties of PH_3BD_3 in the liquid and solid states

PH_3BD_3		PD_3BH_3		PD_3BD_3		Assignment
Solid (25°)	Liquid (35°)	Solid (25°)	Liquid (35°)	Solid (25°)	Liquid (35°)	
	2424 dp	1765 w	1770 dp	1764 m	1764 dp	ν_7
2403 vs	2402 p	1737 vs	1738 p	1736 vs	1736 p	ν_1
2315 w	2315 p					?
1811 w	1811 dp	2418 m	2408 dp	1810 w	1810 dp	ν_8
1718 vs	1715 p	2368 s	2367 p	1724 m, sh	1723 p	ν_2
1612 w	1612 p					impurity
1441 vvw	1441 p					impurity
1366 w	1372 p					impurity
1111 w	1117 dp					impurity
1091 vw	1091 dp	775 w	792 dp	792 w	792 dp	ν_{10}
1021 w	1021 dp	754 w	757 p	728 m	728 p	ν_4
970 vvw		925 vvw				?
		850		855		?
	834 dp	1129 vw	1145 dp	833 vw, sh		ν_9
817 w	815 p	1050 vw		842 w	842 dp	ν_3
				765 vvw	762 dp	?
713 vvw		813 w	813 dp	645 vw	648 dp	ν_{11}
516 s	516 p	552 s	547 p	511 s	512 p	ν_5
460 vw	460 p					impurity
384 w	384 dp	358 m	358 dp	324 w	323 dp	ν_{12}

(Frequencies in cm^{-1})

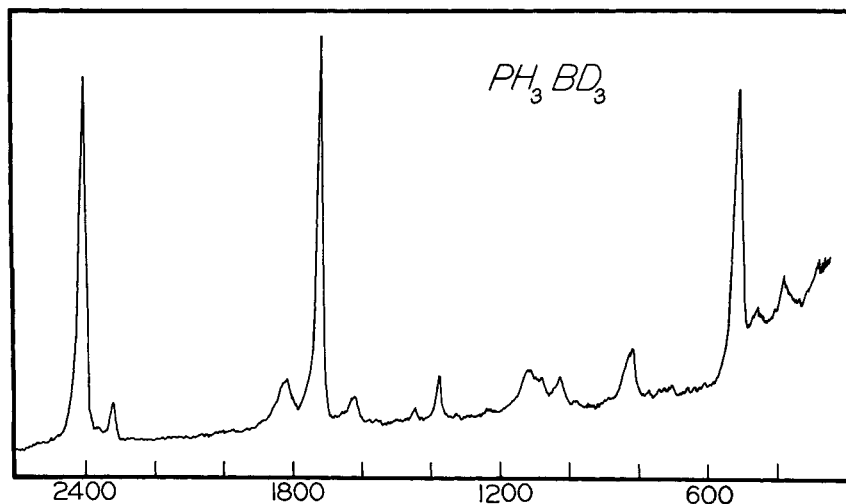


Fig. 1. Raman spectrum of PH_3BD_3 at 25°C.

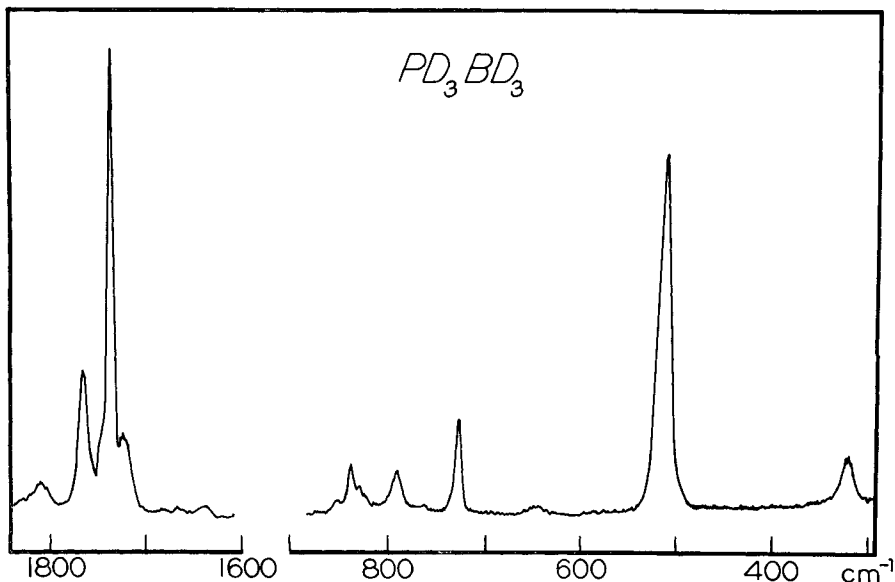


Fig. 2. Raman spectrum of PD_3BD_3 at $25^\circ C$.

Rudolph *et al.* [11] on the basis of their infrared and Raman data proposed assignments for PH_3BH_3 . Sawodny and Goubeau [4], however, questioned some of these assignments on the basis of their force constant calculations and other considerations. The principal points of disagreement involved the symmetric P—H and B—H stretches and the symmetric PH_3 and degenerate BH_3 deformations. The infrared data of Davis and Drake [13] on the deuterium substituted species supported the Sawodny and Goubeau assignments as does the present work. However, several of the Davis and Drake assignments for the deuterated species have been revised as a result of the present study. These changes are limited to the various deformation bands falling in the general region between 750 and 1150 cm^{-1} . Most of the bands in this region are relatively weak in the Raman effect, polarization ratios for the symmetric bands either were difficult to determine or were nearly the same magnitude as those of the depolarized bands, and overlapping was often a problem. The principal evidence for the revised assignments being proposed here, consequently, is based on the results of the normal coordinate analysis. The Davis and Drake frequency assignments could not be fitted as satisfactorily as those being proposed here and the product rule ratios for their assignments also were in significantly poorer agreement with the theoretical values than those shown in Table IV. The final choice of assignments for all four isotopic species is given in Table VI.

4. Normal Coordinate Calculations

Although a wide variety of potential functions are currently employed in carrying out vibrational analyses, the predominant practice is to express these in terms of various

TABLE IV
Product rule ratios for various isotopic species of phosphine-borane
and trifluorophosphine-borane

PRODUCT RULE Isotopes	A_1 class		E class	
	Exptl.	Theoret.	Exptl.	Theoret.
$\text{PF}_3^{11}\text{BH}_3$	1.926	1.970	2.595	2.622
$\text{PF}_3^{11}\text{BD}_3$				
$\text{PF}_3^{10}\text{BH}_3$	1.034	1.043	1.035	1.028
$\text{PF}_3^{11}\text{BH}_3$				
$\text{PH}_3^{11}\text{BH}_3$	1.888	1.938	2.477	2.576
$\text{PD}_3^{11}\text{BH}_3$				
$\text{PH}_3^{11}\text{BH}_3$	1.909	1.938	2.486	2.489
$\text{PH}_3^{11}\text{BD}_3$				
$\text{PH}_3^{11}\text{BH}_3$	3.619	3.764	6.176	6.455
$\text{PD}_3^{11}\text{BD}_3$				
SUM RULE				
$\sum \nu^2(\text{PH}_3\text{BH}_3) + \sum \nu^2(\text{PD}_3\text{BD}_3)$	A_1 class: $2.126 \times 10^7 \text{ cm}^{-2}$		E class: $2.332 \times 10^7 \text{ cm}^{-2}$	
$\sum \nu^2(\text{PH}_3\text{BD}_3) + \sum \nu^2(\text{PD}_3\text{BH}_3)$	A_1 class: $2.130 \times 10^7 \text{ cm}^{-2}$		E class: $2.331 \times 10^7 \text{ cm}^{-2}$	

types of force constants. It has been pointed out [16, 17] that the use of compliance constants provides an alternative method of formulating the vibrational problem which has certain intrinsic advantages. However, the compliance constant approach has not yet found general acceptance and most instances of its use to date have been concerned with small molecules. It appears very desirable that the usefulness of compliance constants in the analysis of the vibrational spectra of larger molecules be explored, both to evaluate the practical aspects of computational procedures and also to explore advantages which these constants may have. In particular, it is desirable to know if compliance constants are more or less transferable than force constants, if they can be more easily correlated with other chemical and molecular properties, and if the effects of the constraints which usually must be introduced into a normal coordinate analysis can be more clearly identified. The answers to these and other questions can only be ascertained by the accumulation of a significant amount of data from a variety of molecules.

The program used for the computations in the present work was a modification of the one described previously from this laboratory for the calculation of force constants [18]. It was written in Fortran IV and adapted for use on an IBM 360/67 computer utilizing virtual storage. The secular equation was expressed in the form $|CK - \phi I| = 0$, where $C = F^{-1}$, $K = G^{-1}$ and $\phi = \lambda^{-1}$, and solved as $CK \cdot L = L\phi$. The L matrix in this case is identical with that in the usual secular equation, $GF \cdot L = LA$. Following symmetrization of the secular equation by the method of Aldous and Mills

[19], the compliance constants were adjusted by a standard iterative damped least squares procedure based on the Jacobian of frequencies with respect to compliance constants. Data for up to eight isotopic species of a given symmetry could be treated at one time, all isotopic frequencies being fitted simultaneously. Preselected compliance constants could be removed from the adjustment process by constraining them to a fixed value, usually zero. Symmetry coordinates and symmetry compliance constants were used as the basis of the present calculations although symmetry factoring was not a specific requirement of the program.

Input data for the program included the observed frequencies, the isotopic G matrices (previously calculated), a trial compliance matrix and a set of weighting factors. The G matrix elements were evaluated from the published microwave parameters using the expressions of Decius [20] and transformed to the symmetry coordinate basis by computer. Symmetry coordinate expressions for a X_3YZW_3 molecule having C_{3v} symmetry have been published previously [18]. The sequence of coordinates is made clear in Table II for the two molecules. Although compliance constants can be calculated without inverting the G matrices [21], matrix inversion is relatively simple and accurate with large computers. Since the redundancies were removed in the transformation to the symmetry coordinate basis, the K matrices were obtained by inversion prior to the computation of the symmetrized secular equation. The selection of an appropriate weighting scheme for the frequencies is always of some concern and various criteria have been recommended in the past. In the case of force constants, weights usually are taken proportional to $1/\lambda$ with an additional factor proportional to the reciprocal experimental error for individual frequencies. Jones [22] has suggested that weights in compliance constant calculations should be proportional to λ^3 to be consistent with the usual force constant weighting scheme. However, experience in the present work showed that weights proportional to λ^2 gave satisfactory results and these factors were then used with individual entries modified where observed values were missing or uncertain.

A frequent and well recognized problem in the calculation of force constants from exclusively vibrational data is that certain constants cannot be determined, even in the favorable case when the number of observed isotopic frequencies significantly exceeds the number of constants to be determined [19, 23]. The investigator usually is made aware of this situation by computational difficulties arising from ill-conditioned equations in the least squares step. In the present study, a comparison was made and the degree of numerical difficulty appeared to be reduced when compliance constants were being calculated compared to when the problem was based on force constants. As a result, computational procedures went relatively smoothly and it was relatively easy to determine which constants were significant, and which should be constrained to zero. Judgment to constrain a constant was made on the basis of an excessively high dispersion, or the fact that the calculated magnitude of the constant was negligible. For both molecules, it was found that only a small number of off-diagonal constants were sensitive and necessary for a satisfactory fit.

It is generally acknowledged that harmonic frequencies rather than the observed

TABLE V

Fundamental frequencies, estimated harmonic frequencies and differences between these values and those calculated by normal coordinate analyses for three isotopic trifluorophosphine-borane species (Experimental values in cm^{-1} for the solid at -180°C)

	$\text{F}_3\text{P}^{11}\text{BH}_3$			$\text{F}_3\text{P}^{10}\text{BH}_3$			$\text{F}_3\text{P}^{11}\text{BD}_3$				
	Exptl.	Δ	Harm.	Δ	Harm.	Δ	Exptl.	Δ	Harm.	Δ	
<i>A</i> ₁ species											
ν_1	2391	-3	2517	0	2395	-2	2521	1	1802	-1	
ν_2	1079	-1	1104	0	1093	-1	1118	-1	854	0	
ν_3	920	0	940	1	920	-2	940	-1	965	0	
ν_4	607	-1	618	0	616	-2	627	-1	578	0	
ν_5	437	0	443	0	439	-3	446	-1	422	0	
<i>E</i> species											
ν_7	2460	-1	2547	0	2470	-5	2563	0	1914	0	
ν_8	1123	-2	1141	0	1127	-1	1145	0	818	0	
ν_9	944	-1	957	0	944	-1	957	0	969	0	
ν_{10}	701	-2	709	-1	709	2	714	1	540	-2	
ν_{11}	370	0	732	0	(370) ^c	-	372	0	364	0	
ν_{12}	197	0	198	0	(200) ^c	-	200	-1	186	1	

^a Temperature correction estimated.

^b Fundamental not observed; value estimated from overtone.

^c Fundamental not observed; calculated value.

TABLE VI

Fundamental and harmonic frequencies, and deviations between assigned and calculated values for four isotopic species of PH_3BH_3 (frequencies in cm^{-1})

	PH_3BH_3				PD_3BD_3			
	Exptl.	Δ	Harm.	Δ	Exptl.	Δ	Harm.	Δ
<i>A₁</i> species								
ν_1	2401	-14	2528 ^a	0	1736	9	1807 ^a	0
ν_2	2363	-7	2490	0	1724	6	1794	0
ν_3	1069	-3	1093	0	842	-1	857	0
ν_4	978	-7	1000	0	728	1	739	0
ν_5	572	-1	580	0	511	5	516	0
<i>E</i> species								
ν_7	2426	-10	2548 ^a	-1	1764	8	1838 ^a	1
ν_8	2408	2	2515	1	1810	-2	1888	-1
ν_9	1144	-1	1168	1	833	0	851	0
ν_{10}	1102	-15	1130	1	792	-2	802	-1
ν_{11}	826	-9	855	1	645	6	654	-1
ν_{12}	447	-1	452	0	324	1	325	0
<hr/>								
	PD_3BH_3				PH_3BD_3			
<i>A₁</i> species								
ν_1	1737	10	1807 ^b	-	2403	-12	2528 ^b	-
ν_2	2368	-2	2490	-	1718	-1	1794	-
ν_3	1050	0	1078	-	817	4	829	-
ν_4	754	4	763	-	1021	2	1026	-
ν_5	552	-2	556	-	516	-3	534	-
<i>E</i> species								
ν_7	1765	8	1838 ^b	-	2424	-12	2549 ^b	-
ν_8	2408	2	2514	-	1811	-1	1889	-
ν_9	1145	0	1167	-	834	1	851	-
ν_{10}	775	16	769	-	1091	-22	1124	-
ν_{11}	813	-20	850	-	713	4	726	-
ν_{12}	358	2	359	-	384	-4	392	-

^a Harmonic frequencies estimated by Dennison's method.

^b Harmonic frequencies calculated from potential function obtained for normal and d_6 species.

anharmonic fundamentals constitute the most significant basis for normal coordinate calculations where potential constants are sought. Experimental difficulties make it difficult to evaluate the harmonic frequencies of any but the simplest molecules and in practice, observed values usually are used. However, harmonic frequencies can be estimated with reasonable accuracy in some cases and when this can be done, the results provide a useful basis for comparison. In the present work, harmonic frequencies were estimated by Dennison's method [24] for the three isotopic species of PF_3BH_3 , and for the two species, PH_3BH_3 and PD_3BD_3 . Dennison's method requires certain assumptions be made regarding the anharmonicities. It was assumed that the anharmonicity coefficient, x_i , was identical for all frequencies of a given class of a given molecule, and that the anharmonicity corrections, $\Delta\nu_j$, were given by $\Delta\nu_j^i = x_i\omega_j \approx x_i\nu_j$, i being

the index for a symmetry class. The estimated sets of harmonic frequencies obtained in this way were fitted with the same potential functions used for the experimental frequencies. The assumptions appeared justifiable since the harmonic frequencies were fitted perfectly. Harmonic frequencies for the mixed species, PH_3BD_3 and PD_3BH_3 , were evaluated from the constants obtained for the PH_3BH_3 — PD_3BD_3 pair. The estimated harmonic frequencies for the two sets of molecules are also shown in Tables V and VI.

4.1. TRIFLUOROPHOSPHINE-BORANE

For this molecule, three off-diagonal constants were needed in each class giving a total of seventeen symmetry compliance constants to fit the twenty nine assigned fundamentals of the three isotopic species. The average percent deviations were 0.24%

TABLE VII
Symmetry compliance constants and force constants for observed and estimated harmonic frequencies of PF_3BH_3

Index	Compliance constants ^a				Force constants ^b		Description
	Observed		Harmonic		Observed	Harmonic	
	<i>C</i>	δ^*	<i>C</i>	δ^*	<i>F</i>	<i>F</i>	
<i>A</i> ₁ class							
1,1	0.308	0.017	0.276	0.004	3.310	3.670	B—H str
2,2	1.898	.037	1.838	0.010	.555	.566	BH ₃ def
3,3	.196	.005	.186	.001	5.093	5.390	P—F str
4,4	.405	.008	.395	.002	2.557	2.597	P—B str
5,5	.749	.018	.727	.005	1.335	1.377	PF ₃ def
1,2	.105	.094	.083	.027	-.189	-.169	
1,4	—	—	—	—	.074	.057	
1,5	—	—	—	—	.001	.001	
2,4	.158	.015	.134	.004	-.216	-.192	
2,5	—	—	—	—	-.003	-.004	
4,5	-.012	.011	-.015	.003	.040	.053	
<i>E</i> class							
7,7	.315	.002	.296	.001	3.173	3.382	B—H str
8,8	2.842	.024	2.746	.007	.354	.366	BH ₃ def
9,9	.181	.001	.176	.000	5.551	5.704	P—F str
10,10	2.665	.031	2.624	.008	.391	.398	BH ₃ rock
11,11	.727	.007	.719	.002	1.434	1.453	PF ₃ def
12,12	2.958	.014	2.930	.004	.338	.341	PF ₃ rock
7,8	.019	.044	-.022	.012	-.021	.028	
7,9	—	—	—	—	.006	-.008	
8,9	.051	.004	.051	.001	-.100	-.106	
10,11	.280	.029	.282	.008	-.151	-.156	

^a Units: $\text{\AA} \text{md}^{-1}$, md^{-1} , $\text{md}^{-1} \text{\AA}^{-1}$.

^b Units: $\text{md} \text{\AA}^{-1}$, md , $\text{md} \text{\AA}$.

* Dispersions: $\delta^2 = \sigma^2 / (J' W J)_{ii}$.

and 0.17% for the A_1 and E classes, respectively. The two sets of symmetry compliance constants for the observed and estimated harmonic frequencies, together with the symmetry force constants obtained by inversion of the compliance matrices, are listed in Table VII. Of somewhat more direct chemical interest are the valence constants obtained from the symmetry constants. In the case of compliance constants, values can be obtained for all the valence coordinates [16, 17] although some values may not be independent; this is not possible for force constants when redundancies are present. Some of the more important valence constants are given in Table IX.

4.2. PHOSPHINE-BORANE

Four off-diagonal constants were retained in the A_1 class of this molecule and two in the E class giving a total of seventeen constants needed to fit the forty four assigned fundamentals of the four isotopic species. The average percent deviations obtained were 0.37% and 0.63% for the two classes, respectively, not quite as satisfactory as for trifluorophosphine-borane but still quite good considering the number of hydrogen

TABLE VIII
Symmetry compliance constants and force constants for observed and estimated harmonic frequencies of PH_3BH_3

Index	Compliance constants ^a				Force constants ^b		Description
	Observed		Harmonic		Observed	Harmonic	
	C	δ^*	C	δ^*	F	F	
<i>A</i> ₁ class							
1,1	0.295	0.002	0.269	0.000	3.394	4.718	P—H str
2,2	.369	.035	.308	.005	3.096	3.505	B—H str
3,3	1.973	.060	1.906	.321	.595	.594	BH ₃ def
4,4	2.304	.037	2.290	.372	.437	.440	PH ₃ def
5,5	.525	.010	.522	.005	1.954	2.009	P—B str
2,3	.296	.076	.201	.036	-.477	-.388	
2,4	—	—	—	—	-.032	-.023	
2,5	—	—	—	—	.137	.151	
3,4	-.158	.023	-.152	.223	.040	.035	
3,5	.152	.026	.206	.026	-.171	-.231	
4,5	-.014	.023	-.046	.005	.000	.025	
<i>E</i> class							
7,7	.295	.003	.270	.000	3.390	3.710	P—H str
8,8	.332	.010	.303	.001	3.015	3.306	B—H str
9,9	2.622	.068	2.533	.010	.382	.395	BH ₃ def
10,10	1.694	.023	1.663	.010	.590	.601	PH ₃ def
11,11	2.853	.085	2.764	.115	.433	.453	BH ₃ rock
12,12	3.007	.070	2.947	.095	.411	.425	PH ₃ rock
8,9	-.024	.109	.005	.017	.028	-.007	
11,12	-1.280	.034	-1.283	0.44	.184	.197	

^a Units: $\text{\AA} \text{md}^{-1}$, md^{-1} , $\text{md}^{-1}\text{\AA}^{-1}$.

^b Units: $\text{md} \text{\AA}^{-1}$, md , $\text{md}\text{\AA}$.

* Dispersions, $\delta^2 = \sigma^2 / (J'WJ)_{ii}$.

TABLE IX
Some valence stretching force and compliance constants for
PF₃BH₃ and PH₃BH₃

Constant	Compliance		Force	
	Observed freq.	Harmonic freq.	Observed freq.	Harmonic freq.
PF ₃ BH ₃				
B—H	0.313	0.289	3.22	3.48
P—F	.186	.179	5.40	5.60
P—B	.405	.395	2.56	2.60
BH, BH	-.002	-.007	.05	.10
PF, PF	.005	.003	-.15	-.11
PH ₃ BH ₃				
B—H	0.344	0.304	3.04	3.37
P—H	.295	.269	3.39	3.71
P—B	.525	.522	1.95	2.01
BH, BH	.012	.002	.03	.07
PH, PH	.000	.000	.00	.00

All units md Å⁻¹.

atoms in the molecule. The pattern of deviations between the observed and calculated values indicated that neglect of anharmonicity was the principal contributor to the discrepancies. Symmetry compliance constants and the derived symmetry force constants are listed in Table VIII. Valence constants of interest are shown in Table IX.

5. Discussion

In the case of both molecules, the revised assignments represent a significant improvement over preceding attempts. This fact plus the fact that the vibrational analyses were appreciably overdetermined are conducive to a greater degree of confidence in the values for the potential constants. Actually, comparison of the values of the stretching constants found here (Table IX) with those published by Goubeau [4] and Berscheid [5, 25] show better than expected agreement, particularly in the values associated with the P—B bond. Alternatively, it might be fair to state that the P—B force constant appears relatively insensitive to minor differences in the rest of the potential function. Differences in sign and/or magnitude in some of the off-diagonal constants between the present and previous values can be attributed to the difference in assignments and the potential functions used. Although the sets of potential constants obtained in the present work are not completely general because constraints were employed, nevertheless the important and significant terms in the potential energy appear to have been identified and we believe the results provide a reasonable approximation to the actual vibrational potential functions of the molecules.

In general, the differences between the constants obtained from the observed (anharmonic) frequencies and the estimated harmonic frequencies are about what one might expect. The largest differences appear in constants associated with the hydrogen atom motions whereas the P—B compliance/force constants are essentially unchanged. The off-diagonal compliance constant connecting the BH₃ deformation and the P—B stretch was found to be smaller for the harmonic frequencies in the case of the PF₃ complex whereas it was larger for the harmonic set in the PH₃ complex. The significance of such a change in opposite directions is uncertain. It may have resulted only because the sets of estimated harmonic frequencies are not quite accurate.

Chemical and thermodynamic data [2, 3] suggest that PF₃ is a slightly stronger donor towards BH₃ than is PH₃ but the difference is small since both complexes are quite weak. It is therefore of interest to note that the P—B bond force constant in PF₃BH₃ is significantly (30%) stronger than in PH₃BH₃. However, the P—B bond in PF₃BH₃ is still a relatively weak bond considering that the P—B distance, 1.836 Å, is one of the shortest P—B distances determined. The P—C bonds in (CH₃)₃PBX₃ complexes, for comparison, are only about 0.02 Å shorter but have a force constant of about 3.1 md Å⁻¹ [26]. To this extent, then, the results seem to bear out the arguments of Rudolph and Parry [2] in their polarizability model that a bond can be short and still not strong. There seem to be no unusual features of the potential function of the PF₃ adduct, such as interaction constants connecting local BH₃ coordinates with those of the PF₃ group, which might be cited as support for the hyperconjugative model. Various authors [8, 12, 27] who have compared P—B bond distances have commented on peculiarities in bond length—stability relationships in phosphorus-boron compounds and it seems clear that the nature of the P—B dative bond is still not fully understood.

Besides the dative bond force/compliance constant, a useful index of the degree of interaction between the acid and base portions of these Lewis complexes is the extent to which the BH₃ group has assumed a tetrahedral *sp*₃ configuration compared to the planar form which is assumed for the free state. Structural data indicate that the degree of interaction of the BH₃ group with the base is nearly identical in these two complexes. Specifically, the H—B—H angle in the PH₃ complex is 114.6° compared to an angle of 115.0° in the PF₃ case while the B—H bond lengths are identical within 0.005 Å. The compliance (or force) constant data, however, show a distinct difference between the two complexes. These results indicate that the BH₃ group in the PH₃ complex is softer and more deformable (compliant) than it is in the PF₃ complex. This may indicate that there is a significant electrostatic interaction in the PF₃ adduct which has the effect of generally tightening up the electron cloud in the BH₃ group even though the donation of the sigma electrons from the phosphorus to the boron is insufficient to convert the configuration around the boron to a completely tetrahedral one. Further, it is of interest to note that recent SCF—MO calculations [28] on PH₃BH₃ and PF₃BH₃ find very little back donation from the BH₃ group into the *d* orbitals on phosphorus as called for by the hyperconjugative model. The electronic structure of the borane group was found to be remarkably similar in the two molecules

but the PH_3 complex was calculated to be somewhat more stable energetically implying that PH_3 is a slightly better donor than PF_3 .

Jones [29] has pointed out that interaction coordinates often give a useful indication of electronic interactions within a molecule. An interaction coordinate, $(I)_k$, is defined as the displacement of a coordinate, I , needed to minimize the potential energy following unit positive displacement of a second coordinate, k , from its equilibrium value. The determination of interaction coordinates is particularly simple in terms of compliance constants [17], the relationship being $(I)_k = C_{Ik}/C_{kk}$. In the case of the molecules considered here, one interaction constant of interest involves the deformation of the BH_3 group as the P—B bond stretches, $(\delta\text{BH}_3)_{\text{PB}}$. In both cases, this interaction coordinate is positive and about 0.3 in magnitude, the positive sign indicating that as the P—B bond lengthens, the BH_3 group tends to flatten out. This behavior appears to be a clear consequence of orbital following during the P—B vibration, the motion most directly related to the dissociation process. Available evidence indicates that analogous interaction coordinates are significant in virtually all Lewis complexes of group III elements whose vibrational spectra have been analyzed.

Finally, in regard to compliance constants, there appears to be some computational advantage in their use and they appear to serve just as well as force constants as a basis for discussion. Further assessment of their utility must depend on the accumulation of more data.

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